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(NASA-TM-77437) CERAMIC FABRICATION PROCESS
BEFORE FIRING-SURFACE TREATMENT OF CERAMIC
POWDER (National Aeronautics and Space
Administration) 23 p HC A02/MF A01 CSCI 11B

N85-17129

Unclas

G3/27 13469

CERAMIC FABRICATION PROCESS BEFORE FIRING-SURFACE TREAT-
MENT OF CERAMIC POWDER

Teruo Tsunoda

Translation of Ceramics, Japan, vol. 18, no. 2, 1983, pp.
152-160.



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON D.C. 20546 MAY 1985

1. Report No. NASA TM-77437		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle CERAMIC FABRICATION PROCES BEFORE FIRING SURFACE TREATMENT OF CERAMIC POWDER				5. Report Date May, 1984	
7. Author(s) Teruo Tsunoda				6. Performing Organization Code	
				8. Performing Organization Report No.	
				10. Work Unit No.	
9. Performing Organization Name and Address SCITRAM Box 5456 Santa Barbara, CA 93108				11. Contract or Grant No. NASA 3542	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546				13. Type of Report and Period Covered Translation	
				14. Sponsoring Agency Code	
15. Supplementary Notes Translation of Ceramics, Japan, vol. 18, no. 2, 1983, pp. 152-160.					
16. Abstract This report discusses surface treatment of powders. Stability of ceramic powders and surfaces, and improvement of moldability are discussed. Characteristics of surface treatment technology are given, such as formation of inorganic surface-treated layers, liquid phase reactions, gas treatment, surface treatment by coupling agents, and the formation of polymer treatment layers. No quantitative explanation is found based on the results of surface treatment.					
17. Key Words (Entered by Author(s))			18. Distribution Statement Unclassified and Unlimited		
19. Security Class. (of this report) Unclassified		20. Security Class. (of this page) Unclassified		21. No. of Pages 23	
				22. Price	

CERAMIC FABRICATION PROCESS BEFORE FIRING-SURFACE TREATMENT OF CERAMIC POWDER

This text discusses surface treatment of powders. Surface treatment has been practically used for many years. However, here we will mainly discuss surface treatment from the points of improvement of the surface and a uniform powder mixture. This field may be very important for the development of fine ceramics.

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Introduction

In discussing atomic arrangement of a single salt crystal by disruption, etc. of molecular rays, it is known that the structure of the surface of the crystal is different from the inside and that some sodium ions shift to the inside, while chlorine ions shift to the outside. The fact that the atoms, ions, and molecules at the surface are located in asymmetric potential sites is one factor in this type of structure.

Powders have a particularly large surface area in comparison to their bulk volume and various disturbances are seen at the surface for the above-mentioned reasons. Furthermore, during powder manufacture processes, for instance, external force is exerted during pulverization, etc. and disorder of the crystal structure is produced. This leads to defects and changes in the chemical composition. Consequently, chemical groups (functional groups) are produced by absorption of air (steam, oxygen, etc) from the atmosphere.

Consequently, when powders are used, it is necessary to determine their surface state in order to use the peculiarities of each powder. A technology for making "reproducible" surfaces and a technology for providing new functions are necessary. This is the purpose of surface treatment. It is necessary to devise new methods for determining the properties of these powder surfaces. This text pertains to these new ideas and methods.

Few works have been published on surface treatment of ceramic particles. This may be due to the fact that there is little information and knowledge on surface treatment or to the fact that no substantial progress has been made in the way of surface treatment. However, the former appears to be due to the latter.

In order to improve the properties of ceramic products, and to develop new products with new functions, the applications in Table 1 have been considered. Therefore, it appears that surface treatment of ceramic particles should ultimately be applied.

*Numbers in margins indicate foreign page number.

Surface treatment of powders is being carried out for various purposes. Therefore, we should explain application of basic technologies to ceramic particles. As was previously mentioned, there have been few examples of surface treatment of ceramics and few reports on the results of these procedures, such as how properties were improved, etc. Consequently, there are few tables and figures and relatively few references. In the future, we would like to see this discussion continued and the conclusions reached in this paper confirmed.

Table 1 Application of Surface Treatment

Purpose of Treatment		Details
Process technology	Prevention of coagulation of crude powder	High polymer layer or nonhygroscopic inorganic layer
	Moldability	Obtain high dispersion into molding binder by using surfactant or nonhygroscopic polymer layer; particles ¹
	Sinterability	Formation of surface with small amounts of sintering agents when necessary; improvement of surface energy, disorder, etc.
Functions	Particle boundary control	Improvement of property reproducibility at particle boundary, treatment for new functions.
	Particle surface	Provide highly selective surface reaction layer.
Application to composite system	Interaction of particles and matrix ²	Provides polymer surface that will react with matrix.

¹Described in edition on "molding."

²Medium in which particles are dispersed.

VIII.1 Purpose of Surface Treatment

1.1 Stability of Ceramic Powders and Surface

There are many times when it is necessary to store crude powders for long periods of time until they are used. When the powder particles coagulate or adhere, the apparent particle diameter during sintering or molding changes and there are various changes in the properties of the mold or sintered unit. It has become necessary to perform surface treatment to prevent coagulation and adherence of fine crude powders. For instance, alumina readily absorbs moisture in comparison to oxide powders and therefore, there is a strong tendency for the particles to coagulate due to the surface water. The formation of a titanium oxide layer on the surface by a technology that will be mentioned later is one method for preventing this type of coagulation.

When deterioration of the powder occurs due to activity of the ceramic powder surface when a polymer material is used for the matrix, it is necessary to carry out surface treatment in order to stabilize the surface of the powder.

1.2 Improvement of Moldability

The quality of the green sheet will have a strong effect on the various properties of the IC ceramic substrate. Although there are various properties that a green sheet must have, among these, the fact that the sheet is smooth and dense and thickness is uniform depends to a large extent on the starting powders.

In general, molding is performed prior to the sintering process in the manufacture of ceramics. There are many cases when slurries of the ceramic powders are made using an organic material whose main component is a polymer. The properties of the slurry have a large effect on moldability and it is therefore necessary to obtain a good slurry.

A slurry superior in moldability is characterized by the fact that the rheology of the slurry is suitable, the powder is uniformly distributed through the slurry as primary particles, it is easy to maintain this type of stable condition, and absorbency and dampness of the slurry are good.

*Details on molding are mentioned in the notes and in the edition on molding.

The organic materials that are used for the above-mentioned purpose during sintering are very combustible and no residue should be found after sintering. It is necessary to select a material that is readily eliminated by combustion. However, it is also important to use the minimum amount of organic material necessary.

In addition to making a slurry by mixing only the organic materials and crude powder, presurface treatment of the powder with the organic material is also effective for satisfying the above-mentioned requirements.

In order to improve moldability, surface treatment should be considered for making fine powders in order to improve fluidity of the powder and to improve moldability.

1.3 Improvement of Sintering Properties

When light-permeable alumina is made, a small amount of MgO is added to adjust the extent of particle growth during sintering. With regard to the amount of MgO that is added, when excess MgO is used, a phase that differs from the refraction coefficient of MgO is produced and permeability is reduced, even though there is an increase in the permeability when the number of air holes is reduced.

Since nitride ceramics, which are in demand as new heat-resistant materials, are difficult to sinter, MgO, Y_2O_3 , etc. are used as sintering agents. However, when too much is added, the strength of the silicon nitride itself at high temperatures deteriorates. A technology for manufacturing nitride ceramics without any additives is needed. This has been studied and at the present time the process whereby products are manufactured under normal pressure is advantageous from the point of cost. In this case, the minimum amount of additive is necessary.

Mechanical strength deteriorates when a sintering agent is added because it is not uniformly distributed throughout the product after sintering. In order to prevent this from happening, the agents should not be simply mechanically mixed with the ceramic powder. The application of a surface treatment technology whereby the ceramic powder is uniformly coated with the minimum amount of agents with a small particle diameter, or whereby the surface of the ceramic powder is coated with a thin film of the agent, is being considered.

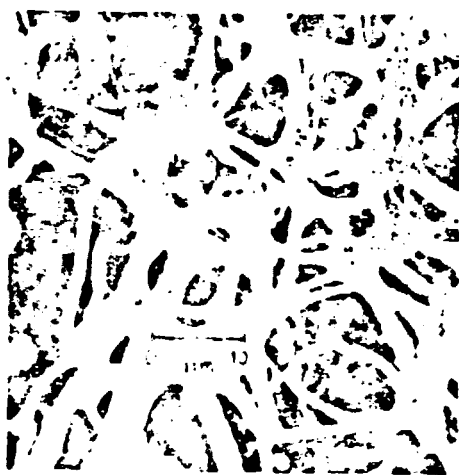
1.4 High Performance of Grain After Sinterings

Various elements are known that use the semiconductive properties of the ceramic. There are elements that use the properties of the crystals themselves and elements that use the surface properties. ZnO varistors, PTC thermistors,

etc., are examples of elements that use the properties of the particle boundaries.

Of these, we will consider ZnO varistors. Although ZnO has high resistance, resistance decreases when a donor position is formed due to excess zinc. When a rare earth element oxide and cobalt oxide are simultaneously added to ZnO, a high-resistance layer is formed near the particle boundary and the voltage-current property becomes nonlinear.

As shown in Figure 1, SnO-Bi₂O₃ varistors often provide good thin layers [1]. When we consider the fact that the precipitate of Bi₂O₃ has a strong effect on the properties of ZnO varistors, it becomes obvious that control of this precipitate layer is very important for controlling variations in properties. Therefore, the ZnO and Bi₂O₃ should not be simply mechanically mixed. They should probably be treated so that a uniform thin layer of the Bi₂O₃ coats the surface of the ZnO particles.



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Figure 1 ZnO Varistor: Secondary Electron Image of Bi₂O₃ Particle Phases After Removal of ZnO Particles by Perchloric Acid Treatment Taken With Scanning Electron Microscope (National Technical Rep., 23(1) 31(1977))

The development of ceramics having new functions is anticipated with the production of various particle boundary layers by surface treatment of ceramic particles.

1.5 High Performance Surfaces

There are catalysts that are used for the high performance surface functions. In this field ceramics have often been used as a carrier that uses fine pores in the surface. However, another role of the carrier is to add catalytic effects to the ceramic itself. The surface layer

has a molecular arrangement that differs from that inside the particle. There are also cases where activity is increased as a defected structure is produced. This is the reason why the particles are used as catalysts. However, the fact that the surface layer has a high activity with surface treatment should also be considered.

There are also cases where the surface functions are employed to the maximum extent, such as in various sensors. In order to obtain a high selectivity in tests on gases by absorption, etc., the surface is being treated with an atomic scale.

1.6 Compounds with Other Materials

There are compounds that are obtained by dispersion of a graphite ceramic superior in heat resistance in a metallic matrix. The properties of the final product improve with an increase in the interaction at the interface between the ceramic powder that is dispersed and the metal matrix. A method for improving this interaction involves improvements of compatibility between the ceramic powder and the metallic matrix. Therefore, a thin layer of the metal should be applied to the ceramic powder by surface treatment.

The final product is pliable when the matrix metal is plastic instead of metallic. It is therefore possible to inexpensively manufacture the final product and increase surface area. Composite materials obtained by dispersion of the ceramic in plastic will probably be seen in the future. For instance, there are ultrasonic sensors in which a ceramic powder is dispersed in a polymer matrix. In order to improve the properties of the final product, interaction between the plastic material and ceramic should be improved. Therefore, we should consider surface treatment of the ceramic powder with a specific polymer material.

VIII.2 Surface Treatment Technology

Judging from materials, the following surface-treatment layers can be produced.

Inorganic surface treatment layers	[thin film treatment layer fine powder coated layer
Organic treatment layers	[Coupling agent layer Surfactant layer Polymer-coated layer Polymer reactive layer

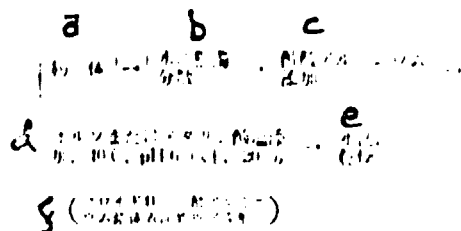


Figure 3 Process By Which a Metallic Phosphate Surface Treatment Film is Made

- Key:
- a. powder
 - b. dispersion in water
 - c. addition of aluminum butyrate
 - d. addition of ortho or meta phosphate, 40°C, pH of 6 or less, 20 minutes
 - e. washing and drying
 - f. (formation of a colloidal aluminum phosphate complex surface treatment layer)

The above-mentioned shows an example of the formation of a treatment layer using a liquid reaction. However, it can also be carried out by accumulation of dissolved inorganic substances on the particle surface.

(c) Formation of a Silicon Oxide Treatment Layer

An example of the production of a silicon treatment layer on metallic particles is shown in Figure 4. In the production of an aqueous solution of a silicate, particles have been dispersed in the solution, an acid is added and dissolved to obtain undissolved silicates that precipitate to the surface of the particles. However, adjustment of the pH of the mixture of the silicate solution and acid is difficult. The conditions of the rate of addition of the acid and stirring to the solution have a strong effect on the properties of the treatment layer. Therefore, the method in Figure 4 is preferred.

The mechanism by which binding properties are improved involves substitution of the aluminum atoms with silicon atoms, which form siloxane bonds in the silicate. These enter the precipitated particles and become anionic due to excess electrons at the substitution sites. It is particularly easy for these groups to bond with metals and alloy powders. Furthermore, the mechanism by which the surface treatment layers are produced by above-mentioned methods in (a)-(c) is a topic for future studies.

These types of treated films can be produced by the following technologies.

2.1 Formation of Inorganic Surface-Treated Layer

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These are used for stabilization of the particle surface, improvement of sintering properties, high performance of grains after sintering, and high performance of particle surfaces.

2.1.1 Gas Treatment

(a) A treated layer can be applied to the surface of a particle using CVD. The sample is placed in a container, which is then placed in a reaction tube. Reactive gas is passed through the tube so that the decomposition product of the reactive gas will accumulate on the powder surface. A great deal of skill is necessary for the method whereby the decomposition product is uniformly coated on the powder in the container.

(b) A treated layer is formed on a powder surface that has been produced by introduction of treatment gas when the powder is produced during the production of a powder from a gas phase. When TiO_2 is produced by pyrolysis of TiCl_4 , metallic vapor is introduced to part of the powder so that a thin metal film is formed on the TiO_2 surface.

(c) Gas etching treatment is also possible. For instance, the surface can be changed by bringing an oxide, hydroxide, carbide, etc. of an alkaline earth metal that is reactive with an acidic gas into contact with an acidic gas that has a water content of 0.1% or less. When hydrogen fluoride gas is brought into contact with calcium carbonate, etc., the surface changes and becomes calcium fluoride. Sulfurous acid gas, phosphoric acid anhydride, chlorides of titanium, aluminum zinc, silica, etc. or fluorides may be used in the treatment.

2.1.2 Liquid Phase Reactions

A treatment layer may be formed by accumulation of an inorganic synthetic reactive substance on the surface of the powder. Various types of inorganic synthetic reactions are known. Therefore, any treatment layer may coat the particle surface. However, the production of a uniform layer is difficult.

In general, reaction solvents contain a large amount of water and therefore cannot be applied to hygroscopic or hydrolytic powders. The manufacture of a layer using a reaction of an organic complex in a solvent and then surface treatment by heating, etc. should be considered.

*Chemical Vapor Deposition: refer to section V.

(a) Example of Production of Oxide Treatment Layer

The simplest example is the method shown in Figure 2, whereby an aluminum oxide or titanium oxide film is formed on the surface of titanium oxide. TiCl_4 , TiI_4 , TiBr_4 , titanium sulfate, tetraethyltitanate, tetratitanate butyrate, etc. are known as materials for making the titanium oxide film. $\text{Al}(\text{OH})_3$, AlCl_3 , aluminum sulfate, tributoxyaluminum, etc. are known as materials for making the aluminum oxide film.

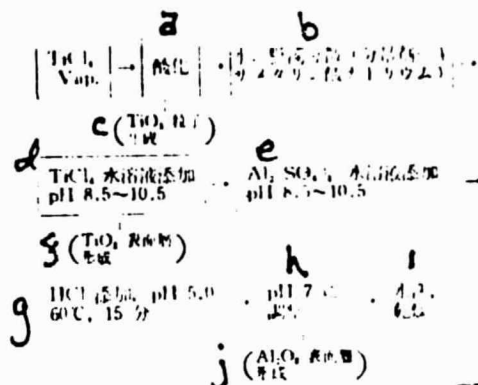


Figure 2 Process By Which A Surface Treatment Layer of TiO_2 or Al_2O_3 is formed on the surface of TiO_2 Particles

- Key:
- a. oxide
 - b. suspension (sodium salt in dispersant)
 - c. TiO_2 particles produced
 - d. TiCl_4 solution added
 - e. $\text{Al}_2(\text{SO}_4)_3$ solution added
 - f. TiO_2 surface layer formed
 - g. HCl added, pH 5.0, 60°C , 15 minutes
 - h. adjusted to pH of 7
 - i. washed and dried
 - j. Al_2O_3 surface layer produced

(b) Formation of Metallic Phosphate Treatment Layer

The method whereby metallic phosphate polymeric film is made is shown in Figure 3 as an example of a complex treatment film. Furthermore, light permeability is used in the reaction monitor. When ammonium fluoride, etc. is added to the slurry, the fluoride ions, etc. enter the treatment layer.

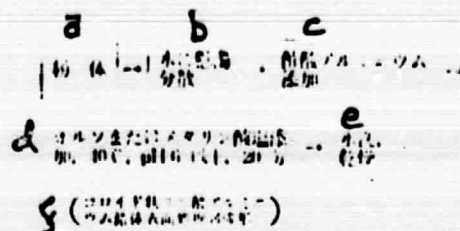


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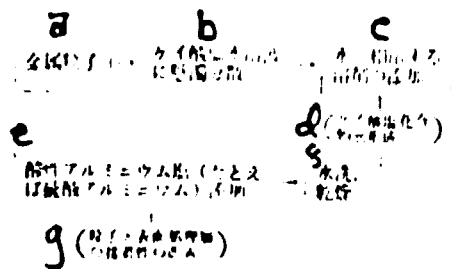


Figure 4 Process By Which A silicate Surface Treatment Layer is Produced on Metallic Particle Surfaces

- Key:
- a. metallic particles
 - b. suspension in silicate aqueous solution
 - c. addition of solvent that is compatible with water
 - d. (formation of silicate compound layer)
 - e. addition of acidic aluminum salt (for instance, aluminum sulfate)
 - f. washing and drying
 - g. (improvement of binding ability between particles and surface treatment layer)

2.2 Surface Treatment by Coupling Agents

The strength of composite materials, such as fiber glass-reinforced plastics, is related to the presence of strong bonds between the filler fibers and the plastic which forms the matrix. The surface of the filler is chemically treated to make these strong bonds. The treated materials used at this time are coupling agents. Typical coupling agents are called silane coupling agents and have the structure of $\text{RSi}(\text{OR}')_3$. The R and OR' groups are shown in Table 2.

Next, the function of the silane coupling agents are shown in Figure 5. A strong bond is formed between the powder and polymer via the coupling agent molecules. A comparison of the case where a glass powder treated with a silane coupling agents is filled with a polymer and the case of an untreated material is shown in Figure 6. The treated glass powder adheres to the polymer, while there is no adherence between the untreated glass powder and the polymer.

The process of treatment using a silane coupling agent is shown in Figure 7.

As can be seen from the above-mentioned, the method of selection of the coupling agents should be based on

selection of a chemical structure where the functional group R in the coupling agents molecules reacts with the polymer.

Examples of coupling agents used for these purposes are given below.

Silane coupling agents

Organic titanium coupling agents

(i₄o PRO)₄Ti; tetraisopropyltitanate,

(nBuO)₄Ti; tetrabutyltitanate

(C₁₆H₃₁O)₄Ti; tetrastearylitanate

Isopropoxytitanium stearate

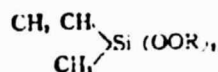
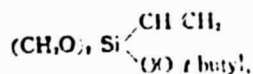
Titanium lactate

Chromium coupling agents

Volan (du Pont)

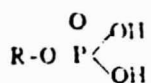
Valchrome 5015 (Valchem)

Syrlperoxides



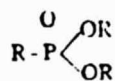
Organophosphate Coupling Agents

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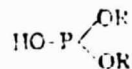
R: エチル, プリル, イソ
アミル基

R; ethyl, butyl,
isocanyl groups



R: メチル, エチル, プチ
ル, 2-エチルヘキシル,
フェニル

R; methyl, ethyl, butyl,
2-ethylhexyl, phenyl



R: メチル, エチル, イソ
ブチル, オクチル

R; methyl, ethyl, iso-
propyl, octyl

Table 2. Typical Silane Coupling Agents

R	OR'	結構式	化学名	適用材
$\text{CH}_2=\text{CH}-$	$-(\text{OC}_2\text{H}_5)_3$	$\text{CH}_2=\text{CH}-\text{Si}(\text{OC}_2\text{H}_5)_3$	d ビニルトリエトキシラン	j アクリル, ポリ エチレン, ポリ プロピレン, 塩化 ビニル, 塩化 ビニル, 塩化 ビニル
$\text{CH}_3-\text{C}(\text{CH}_3)=\text{C}(\text{OCH}_3)-\text{CH}_2-\text{CH}_2-$ O	$-(\text{OC}_2\text{H}_5)_3$	$\text{CH}_3-\text{C}(\text{CH}_3)=\text{C}(\text{OCH}_3)-\text{CH}_2-\text{CH}_2-\text{Si}(\text{OC}_2\text{H}_5)_3$ O	e ガンマ-メタクリロキシプロピルトリメトキシラン	k フェノール, エポキシ, アクリル, ポリ エチレン, ポリ プロピレン, 塩化 ビニル, 塩化 ビニル, 塩化 ビニル
$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$	$-(\text{OC}_2\text{H}_5)_3$	$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{Si}(\text{OC}_2\text{H}_5)_3$	f ガンマ-アミノプロピルトリメトキシラン	k フェノール, エポキシ, アクリル, ポリ エチレン, ポリ プロピレン, 塩化 ビニル, 塩化 ビニル, 塩化 ビニル
O $\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2-$	$-(\text{OC}_2\text{H}_5)_3$	O $\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2-\text{Si}(\text{OC}_2\text{H}_5)_3$	g ベータ-3,4-エポキシシクロヘキシルエチルトリメトキシラン	k フェノール, エポキシ, アクリル, ポリ エチレン, ポリ プロピレン, 塩化 ビニル, 塩化 ビニル, 塩化 ビニル
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCH}_2\text{CH}_2\text{CH}_2-$ O	$-(\text{OC}_2\text{H}_5)_3$	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{OCH}_2\text{CH}_2\text{CH}_2-\text{Si}(\text{OC}_2\text{H}_5)_3$ O	h ガンマ-グリシドキシプロピルトリメトキシラン	k フェノール, エポキシ, アクリル, ポリ エチレン, ポリ プロピレン, 塩化 ビニル, 塩化 ビニル, 塩化 ビニル
$\text{HS}-\text{CH}_2\text{CH}_2\text{CH}_2-$	$-(\text{OC}_2\text{H}_5)_3$	$\text{HS}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{Si}(\text{OC}_2\text{H}_5)_3$	i ガンマ-メルカプトプロピルトリメトキシラン	k フェノール, エポキシ, アクリル, ポリ エチレン, ポリ プロピレン, 塩化 ビニル, 塩化 ビニル, 塩化 ビニル

- Key:
- a. Structural formula
 - b. Chemical name
 - c. Polymer used
 - d. Vinyltriethoxysilane
 - e. Gamma-methacryloxypropyltrimethoxysilane
 - f. Gamma-aminopropyltriethoxysilane
 - g. beta-3,4-epoxycyclohexylethyltrimethoxysilane
 - h. Gamma-glycidoxypropyltrimethoxysilane
 - i. gamma-mercaptopropyltrimethoxysilane
 - j. alkides, polyethylene, polypropylene urethane
 - k. phenols, epoxys, melamines, nylon, polyimides, polycarbonates
 - l. butyls, epoxyphenols, vinyl chloride, epi-chlorhydrin
 - m. neoprene, polysulfides, polybutadiene, urethane

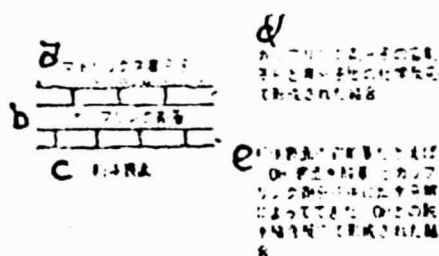


Figure 5 Function of Coupling Agents

- Key:
- a. matrix polymer
 - b. coupling agent layer
 - c. powder surface
 - d. bond formed by chemical reaction between functional R group and polymer
 - e. bond formed by reaction between $-\text{OH}$, which is made by hydrolysis in coupling agent molecules and functional group at powder surface, for instance, $-\text{OH}$ (surface hydroxide group)

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Agent-treated glass powder



Untreated glass powder

Figure 6 Results of Studying Binding with Polymer in Case
of Silane Coupling Agent-treated and Untreated Glass Powder
(Diameter of Several μm) using Electron Microscope
(Nihon Unika Materials)

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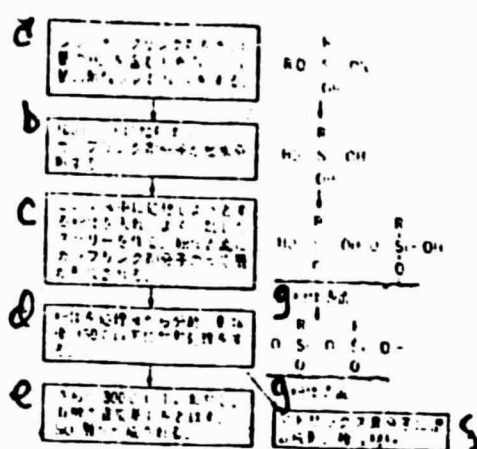


Figure 7 Coupling Agent Treatment Process

- Key:**
- The silane coupling agent is dissolved in water (containing a trace of HCl) or a solvent (containing a small amount of butyric acid).
 - Heat to 100°C or less
Coupling agent is pyrolyzed.
 - The powder is added and dispersed to form a slurry.
A reaction layer of the coupling agent is formed on the powder surface.
 - The powder is (illegible) from the treatment solution and dried and is then heated at 150 C or less.
 - The powder is heated again to 300 C or less to (illegible) the organic functional group R. An SO film is formed
 - Complex material formed by mixing in matrix polymer.
 - powder surface

2.3 Formation of Polymer Treatment Layer

One purpose of the treatment here is to coat the surface with a polymer material as a protective layer that will protect the powder against humidity, etc. When a slurry is made for the formation of the crude powder, a small amount of polymer compound should be added as the binder. When the slurry is made, the polymer is not simply added. It should be added so that the surface is pretreated with the polymer. A composite material is obtained by adding a ceramic powder to a polymer matrix. In order to improve mechanical strength, the interaction between the polymer matrix and ceramic should be maintained. The surface graft method is a method which provides good results by coating the powder with a polymer material that interacts strongly

or by reacting the polymer material with the surface of the ceramic powder. These methods are summarized in Table 3.

2.3.1 Polymerization of Absorption Monomer

A monomer is dissolved in a solvent. The powder is added to this to produce the slurry and the dissolved monomer is absorbed by the ceramic powder. Then the powder that absorbs the monomer is separated from the slurry. The monomer is polymerized with γ -ray light, ultraviolet light, etc., to form a polymer layer. For instance, hydrogen carbide is absorbed by silica and activated charcoal. The hydrocarbon that is absorbed is polymerized when irradiated with γ -rays. Thus, a polypropylene layer is formed on the powder surface. When rinsed with xylene, 2-4% of the polypropylene remains. When γ -rays cannot be used, polymerization can be performed by ultraviolet rays, etc. A photosensitizer may be added to accelerate the reaction with ultraviolet rays. Monomers can also be polymerized by radiation and light. In addition, the method whereby the monomer is polymerized by heat while adding a polymerization solvent such as benzoyl peroxide, etc., is also used. Depending on the type of monomer, polymerization with heat only is also possible.

A treatment example will be shown. It appears that the value is markedly improved by improvement of the final product when a metallic alloy powder of iron, iron-cobalt, nickel, etc., is used as the magnetic powder for magnetic tapes or disks. However, the powder itself actually oxidizes because of the increase in surface activity. Furthermore, there are powders that are difficult to use because there is a chance that they will catch on fire when added to an organic binder. In order to protect the surface, surface treatment must be studied. The formation of a polymer layer on the surface has been proposed.

γ - Fe_2O_3 or Fe_3O_4 is reduced for 3 hours in hydrogen at 350°C to produce iron powder. This is cooled to room temperature while avoiding contact with air. Then it is added in a benzene solution. The monomer used at this time is tetraethylene glycol dimethacrylate.

The monomer concentration is within the range of 1:6 to 1:15 (monomer:benzene ratio). When set aside, the monomer is absorbed by the powder. Next, the slurry is placed under reduced pressure at 60°C to vaporize the benzene. The dissolved monomer adheres to the iron particles to form a considerably thick monomer layer on the particle surface. This layer is polymerized to form a polymer layer. Next, this iron powder is added to mineral oil (solvent in which the monomer will not dissolve, heated to a high temperature) and is then stirred while being heated to

110°C. Polymerized film is formed in 4 hours. This is then filtered to separate the mineral oil and iron powder. The remaining mineral oil is washed off with hexane. A polymer film is thereby made from the monomer.

Table 3. Formation of Polymer Treatment Films

Method	Details	Process	Features
Polymerization of absorbed monomer ¹	Polymerization of absorbed monomer	Monomer-solution-powder suspension-vaporization of solvent-suspension insolvent-heating-powder separated-drying	Powder and polymer not bonded
Use of mechanical effects ²	Absorption of polymer or monomer on surface activated by pulverization	Powder mixed with monomer or polymer-pulverization-powder separation-solvent rinsed-dried	Chemical absorption of polymer on powder surface
Use of graft reaction ³	Reaction under increased pressure after mixing polymer and powder	Mixing of powder & polymer-heated-pressure increased-solvent washed-dried	Reaction between powder surface and polymer
Use of phases	Polymer dissolved in solution precipitates to powder surface	Polymer solution prepared-powder suspension-polymer dissolved - separated by various methods-powder separated-dried	Adherence of polymer to powder surface

¹ Low molecular weight prior to polymerization	(CH ₂ CHCl) _n	is a monomer with vinyl chl ride	CH ₂ CHCl
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2. Lattice defects, are produced on the powder surface by pulverization. The powder is activated and readily reacts with other substances. The mechanical force is converted to chemical energy.

3 The polymer reacts with other substances



Polymer	Monomer or polymer	Graft
	This is now a powder	

2.3.2. Application of Mechanochemical Effects

Powders display a new surface when pulverized or ground. This new surface is very reactive, because it has crystal defects. This type of powder uses the chemical activity of the new surface.

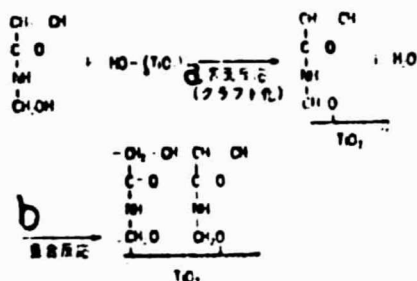
When a polymer or monomer are placed in a pulverizer with a powder that is to be surface treated and mechanical force is applied, the powder develops a new active surface with pulverization. The monomer is absorbed and, when polymerized by the activity of the surface, a polymer layer is produced.

For instance, when a styrene emulsion is added to the calcium carbonate during pulverization, 1-1.5% of styrene bonds to the surface per powder weight.

2.3.3. Formation of Treatment Layer by Graft Reaction

The treatment layer is made by reacting the functional group of the particle surface with the polymer. An oxide powder, such as silica, titanium oxide, or aluminum oxide chemically absorbs water and, as a result, a hydroxyl group is found on its surface. Part of the surface produces SiO_x with SiC when silicon carbides are used. As a result, the surface has a hydroxyl group. The surface becomes molybdenum trioxide when molybdenum disulfide is used and a hydroxyl group is similarly formed on the surface.

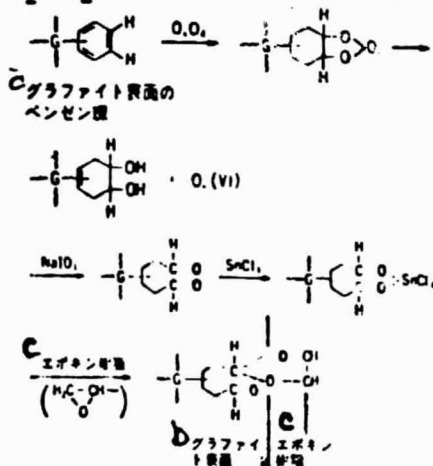
The functional groups that will react with the polymer are generally hydroxyl groups. For example, TiO_2 reacts with methylol acrylamide. When TiO_2 is dried for 1 hour at 100°C in oxygen and is added to the molten methylol acrylamide at 80°C , which is then heated in an autoclave for approximately 10 hours, the following reaction (grafting) occurs:



Key: a. surface reaction (grafting)
b. polymerization

A polymer layer is formed on the TiO_2 surface. This product will thoroughly disperse in organic solvents.

When there is no functional group on the particle surface, grafting does not occur. An example of the graphite will be shown. When graphite is treated with oxminium oxide, hydroxyl groups form in a ring near the graphite surface. Next, when this is treated with NaIO_4 , the hydroxyl group changes to a carbonyl group. This carbonyl group acts as a functional group during polymer treatment. Next, when this is reacted with SnCl_4 , the carbonyl and SnCl_4 formed a surface complex. The reaction of the complex results in graphitization of the graphite surface by the epoxy. This reaction is shown below.



Key: a. benzene ringe on graphite surface
b. graphite surface
c. epoxy resin

The surface-treated graphite disperses thoroughly in the epoxy resin.

2.3.4 Treatment Using Phase Sparation

(a) Method that Uses Water as Solvent

Water-soluble polymers can be separated to the particle surface by adding an electrolyte or by adding a solvent that mixes with water, such as alcohol or acetone. The following polymers can be used.

(1) Natural polymers: gelatin, caseine, Arabia gum, butyric acid starch, hydroxystarches, amino starches, methyl ceullulose, hydroxyethylcel ulose, hydroxy methyl cellulose, etc.

(2) Synthetic polymers: polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylate soidum, polyacrylamide, polyethylene oxide, polyethyleneimine, ionene-type polycations, polymeric surfac ants, etc.

There are often times when water is used for ceramic molding and green sheet manufacture. Th use of the above-mentioned water-soluble polymers should be restricted to the type of surface treatment

(b) Use of Water Separation of Organic Solvents

A powder is supended in an organic solvent and then a polymer is added and mixed. Next, the polymer produces a treatment film on the surface of the powder because it will not dissolve. The method whereby a solvent is added that is soluble with regard to the polymer, the method whereby another polymer is added that will separate the polymer, the method whereby the polymer is separated by heating, etc. are used.

Conclusion

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Systematic research has not been carried out on the correlation between the properties of the final product and the surface treatment of the ceramic powder. Therefore, there have been no quantitative explanations of the results of surface treatment. Moreover, we anticipate surface treatment to be used to a considerable extent in the future and therefore, it should ultimately be studied.

In conclusion, the author invites the reader to review the references for further information of surface treatment technology. [2]

References

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- [2] Koseki and Kakuda: Powder Surface Chemistry, Nikkan Kogyo Publishers (1975).

About the Author:

Teruo Tunoda completed his Ph.D. studies at the University of Tokyo in 1961. In the same year, he began working for Hitachi Central Research Laboratories. He has been a member of the 1st Research Department, a member of the General Research Department, and Head of the 1st Research Department. He is currently a member of the Main Research Department.